”INVESTIGATIONS ON THE CHARACTERISTICS OF MANGANESE BRONZES WITH SILICON ADDITIONS”

A

Long Synopsis for Doctor of Philosophy Thesis

SUBMITTED TO

REGISTRAR (EVALUATION), MANGALORE UNIVERSITY

MANGALAGANGOTHRI-574199, KARNATAKA, INDIA

Submitted by

K. PRABHAKARA

(Reg. No. 166141304)

Under the guidance of

Dr. R KESHAVAMURTHY

Professor& HOD

Department of Mechanical Engineering

Shavige Malleshwara Hills, Kumarswamy Layout

Bengaluru-560078

Dr. D Premachandra Sagar Centre for Advanced Materials

Shavige Malleshwara Hills, Kumarswamy Layout

Bengaluru-560078

CERTIFICATE

Certified that the thesis work entitled **"INVESTIGATIONS ON THE CHARACTERISTICS OF MANGANESE BRONZES WITH SILICON ADDITIONS" carried out by me Mr. K. Prabhakara** (Reg No.166141304), a Research Scholar of Ph.D Programme in Materials Science. Dr. D. Premachandra Sagar Centre for Advanced Materials, Dayananda Sagar College of Engineering, Bengaluru in partial fulfilment for the award of DOCTOR OF PHILOSOPHY of Mangalore University, Mangalagangothri, during the year 2021-2022. To the best of my knowledge the work reported in this thesis has not been submitted by me elsewhere for the award of any degree and is not repetition of the work carried out by others.

K. PRABHAKARA

Name & Signature of the Candidate

To the best of our knowledge, the above statement made by the candidate **K. PRABHAKARA (Reg No. 166141304)** is true.

Name & Signature of Guide

Dr. R. Keshavamurthy

Professor & Head

Mechanical Engg. Dept., DSCE

Dr. D.Premachandra Sagar

Centre for Advanced Materials,

Shavige Malleshwara Hills, Kumaraswamy Layout

Bengaluru-560078

Professor & HOD
Department of Mechanical Engineering
Dayananda Sagar College of Engineering
Kumaraswamy Layout, Bangalore - 560078

Name & Signature of Head of Research Centre

Dr. K. S. Anantharaju

Director, Dr. D.Premachandra Sagar

Centre for Advanced Materials,

Shavige Malleshwara Hills, Kumaraswamy Layout

Bengaluru-560078

Dr. K.S. Anantha Raju
Director
Dr. D. Premachandra Sagar Centre
for Advanced Materials
DSCE Campus, Bengaluru 560 078.

Dr. C. P. S. PRAKASH
Principal
Dayananda Sagar College of Engg.
Bengaluru-560078

Dr.C.P.S.Prakash,M.Tech,Ph.D
Principal
Dayananda Sagar College of Engineering
Kumaraswamy Layout, Bangalore - 560078.

Dr. MANJUNATH PATTABI
Chairman BOS/DOS
Dept. of Materials Science, Mangalore University
Mangalagangothri

SYNOPSIS

Designers have been selecting Copper base alloys from times immemorial as bearing materials as the structure is ideal for mating surfaces. The traditional copper alloys are Copper Tin Bronzes, Leaded Tin Bronzes, Aluminum bronzes and Manganese Bronzes. The selection of the alloy depends on functional conditions of load and lubrication.

High tensile brasses or Manganese Bronzes were first developed about 135 years ago and mainly for Sea Water Corrosion resistance applications. These alloys have hardly undergone any change even while their use has extended into high structural strength applications. The strength of Manganese Bronze is comparable to that of low carbon steel, has good wear resistance and superior corrosion resistance. Manganese Bronzes are also known as High tensile brasses and High strength yellow brasses. These are complex alloys with copper and zinc as the major elements and with small additions of Aluminium, Iron and Manganese. These elements have a tendency to increase the strength and wear resistance of Copper-zinc alloys. The addition of silicon is generally to improve the strength, lubricity and corrosion resistance of the alloy.

The addition of different elements like Al, Fe, Mn and Si alter the room temperature properties as these elements have effects similar to zinc to varying degrees. The Chemistry of Manganese Bronzes show presence of Aluminum, Manganese and Iron for strengthening the alloy. The zinc percentage is substituted with zinc equivalent in order to pr edict the presence of phases at room temperature. In practice, it is observed that a zinc equivalent between 47% and 49% will result in desired properties without brittleness. With the need to keep zinc as low as possible and add elements which will increase apparent zinc to the desired range of zinc equivalent, small additions of Fe, Mn and Al are made. Zinc content above 28% may result in dezincification in corrosive environment and hence silicon is added to provide the necessary resistance to corrosion. Further Silicon in right ratio with Manganese is needed to form Manganese Silicide particles which enhance wear resistance of the alloy.

The mechanical properties of the alloys are a consequence of the room temperature microstructure which in turn depends as the chemistry and the cooling rate. As all the added element have an effect on mechanical properties, it is critical to set aim points for each element within the specification range to obtain the required microstructure. The properties in turn depend on the microstructure. The Cu-Zn equilibrium is binary and yet it is possible to calculate the zinc equivalent (ZE) of complex alloys with factors for each element.

Copper-Zinc equilibrium diagram shows room temperature microstructures can vary from the ductile alpha phase to strong beta phase and brittle gamma phase and a combination of alpha, beta and gamma phases.

The intent of the alloy development here is to ensure that the zinc equivalent does not exceed fifty and the bottom limits of the chemistry also meet the property valves without brittleness even in fast solidification processes like Permanent Mould and Shell Moulding.

The alloys developed here will withstand loading pressures upto 200Mpa, be highly wear resistant and can be subjected to high shock loading. They can be employed for applications under high loads and moderate surface loads. The formation of manganese silicide particles in a matrix of alpha + beta phase composition results in a high hardness ration of 10:1. The high hardness ration along with a low coefficient of dry friction is the reason for the excellent wear resistance.

This Research details the development of High Tensile brass or Cast Manganese Bronzes alloys with Silicon whose zinc equivalent will not exceed 50% out yet possess a high structural strength. The alloy has the potential to substitute high Aluminum Bronze and Tin Bronze alloys which are more expensive.

The survey of available literature covers in detail about the importance of zinc equivalent and the purpose of optimizing it to get the correct microstructure in the alloy.

- The main objectives of this Research has been to develop High Tensile Brasses or Manganese Bronze Alloys with Silicon as an effective alternate for the more expensive Nickel Aluminum Bronzes and Tin Bronze alloys for bearing and wear resistance applications and to study their functional characteristics by Mechanical Property correlation optical/electron microscopic studies, Wear Behaviour, Heat treatment studies for grain refinement.
- It has been the objective of this investigation to maintain zinc equivalent below 50%.
- This investigation has highlighted Composition, Casting characteristics like flow (fluidity), Hot tearing and grain refinement.
- It has been the main objective of this work to arrive at alloys with a zinc equivalent through an optimum microstructure and yet retain the high mechanical properties.
- It has also been the objective of this investigation to make reasonable estimate the performance of Manganese Bronze alloys with Silicon.

This investigation has examined the mechanical and tribological performance of the High Tensile Brasses or Manganese Bronzes with Silicon additions and related these to the

composition and microstructure of the alloys. The objective of this investigation has been to refine recrystallized grains of the alloys from an approach of material properties and to clarify the mechanism of such grain refinement.

ACKNOWLEDGEMENTS

I avail this opportunity to extend my deep sense of gratitude to my guide Dr. R. Keshavamurthy, Professor and Head of the Department of Mechanical Engineering, Dayananda Sagar College of Engineering, Dr. D. Premachandra Sagar Centre for Advanced Materials, Shavige Malleshwara Hills, Kumaraswamy Layout, Bengaluru-560078, for his invaluable guidance, encourage unstring efforts and meticulous attention throughout the course of this work. His impressive knowledge, direction, devotion to work, support and human qualities have been a source of inspiration and a model for me to follow. He is not only a great mentor but also has been main prime mover and chiefly instrumental in my Ph.D Programmes. But for his constant vigil and help in my research, I would not have come so far in my programme.

I would also like to convey my sincere gratitude to Dr. K. S. Anantharaju, Director, Dr. D. Premachandra Sagar Centre for Advanced Materials, Shavige Malleshwara Hills, Kumaraswamy Layout, Bengaluru-560078, and also Professor and Head of the Department of Chemistry, Dayananda Sagar College of Engineering, who has been mainly responsible for establishing this Research Centre at Dayananda Sagar College of Engineering and tutoring / mentoring me with all the courses/examinations taken at Mangalore University, Department of Materials Science, Mangalagangothri qualifying me for Ph.D degree in that University. But for his constant support, I would not have come so far in the program.

I would like to express my sincere gratitude to Dr. C. P. S. Prakash, Principal, Dayananda Sagar College of Engineering for his constant inspiration and encouragement throughout my Research work.

I am deeply indebted to Dr. Manjunatha Pattabi, Professor and Chairman of the Department of Materials Science, Mangalore University, Mangalagangothri for his constant support and encouragement throughout the programme.

I would like to thank specially Dr. P. Sriram, Chairman, Rapsri Engg. Products Private Limited, Bylekuppe Village, Harohalli, Kanakapura Taluk, Ramanagara District, Karnataka for all the kindness and generosity he showed in accompdating and interacting with me during the synthesis and initial characterisation of the Manganese Bronze Castings in his factory. I will not be exaggrerating in saying that Dr. Sriram of RAPSRI Engg. Products Private limited has been mainly instrumental in my success in the Ph.D program so far next to only my guide Dr. R. Keshavamurthy, Professor and Head of the Department of Mechanical Engineering, Dayananda Sagar College of Engineering.

I would like to express my deep gratitude to the Science and Engineering Research Board (SERB)-Government of India, New Delhi, for funding me a Project on Synthesis and Characterization of High Strength Manganese Bronzes with Silicon Additions" along with RAPSRI Engg. Products Private limited, Harohalli under Industry-Institute interaction for a period of three years.

I thank my colleagues Mrs. Kavya. J.T of the Department of Automobile Engg. Mr.Abishek, and Mr. Ahobala of Mechanical Engineering Departmen,. Mrs. Mamatha. R of the Dept. of Mechanical Engg. Mrs.Padmaja of Industrial Engg and Management, Mr.Krishnamurthy and Mr.Kaushik of Rapsri Engg for their assistance during my Research work.

Finally, I will be failing in my duty if I do not express my sincere thanks to my sincere thanks to my ever loving wife Mrs. Pushpa Prabhakar for her keen interest in my Ph.D Program right from the beginning and the necessary support offered. But for her constant support and encouragement, I would not have completed this programme. My special thanks are also due to my son Mr. Prithvi Bhushan Prabhakar and his wife Mrs. Chaitra Prithvi Bhushan for their encouragement.

Lastly, I would like to thank all those who supported me in any respect during the completion of this research work.

NOMENCLATURE

^{O}c	:	Degree Centrigrage
Al	:	Aluminium
Mn	:	Manganese
Si	:	Silicon
Zr	:	Zirconium
Fe	:	Iron
MnSi	:	Manganese Silicide
Cu	:	Copper
Zn	:	Zinc
-Phase	:	Alpha Phase
-Phase	:	Beta Phase
-Phase	:	Gamma Phase
-Phase	:	Kappa Phase
HTB1	**:**	**High tensile brass**
		Cu - 55.0%Min
		Fe - 0.5-2.01%
		Mn - 3.0% max
		Al - 2.5% max
		Ni - 1.0% max
		Pb - 0.5% max
		Sn - 1.5% max
		Zn – reminder
HTB2	**:**	**High tensile brass**
		Cu - 55.0%Min
		Fe - 0.5-2.5%
		Mn - max 3.0%
		Al - max 5.0%
		Ni - max 2.0%
		Pb - max 0.5%
		Sn - max 0.5%
		Zn - reminder

2 Phase – gamma two phase

KI - Kappa one phase

KII - Kappa two phase

KIII - Kappa three phase

KIV - Kappa four phase

Wt% - Weight percentage

CFS - Corrosion Fatigue Strength

SM - Shell moulded

PM - Permanent moulded

ASTM B 505 955 HT - Heat Treatment specification

ApparentZinc(AZ_n)=%ZN+6(%Al)+0.9(%Fe)+0.5(%Mn)+1(%Pb)+2(%Mg)+2(%Sn)+10(%Si)-1.2(%Ni)

$$\text{Zinc Equivalent (ZE)\%} = \frac{\text{Apparent Zinc\%}}{\text{Copper \% + Apparent Zinc \%}}$$

C67300 HT - Cast Manganese Bronze which can be Heat treated

C86100 – C86800 - Strongest as – cast copper base materials-Manganese Bronze (Cu-Zn-Fe-Al-Al-Mn alloys)

IACS - International Annealed Copper Standard

SAE CA673 - Forged Silicon Manganese Bronze

SAE 65 - Chill Cast Tin Bronze

SAE CA 67B - Forged Manganese Bronze

SAE CA 624 - Forged Aluminum Bronze

C 95500 - Aluminum Bronze

C 93700 - Leaded Bronze

DM Water - De mineralised Water

BQS04 - Barium Sulphate

Na_204 - Sodium Sulphate

$Pb0_2$ - Lead Oxide

Pb_2S0_4 - Lead Sulphate

TABLE OF CONTENTS

	DESCRIPTION			Page No.
	CERTIFICATE			I
	SYNOPSIS			II
	ACKNOWLEDGEMENT			VI
	NOMENCLATURE			VIII
	TABLE OF CONTENTS			X
	LIST OF FIGURES			XII
	LIST OF TABLES			XIV
CHAPTER I	INTRODUCTION			1
CHAPTER II	LITERATURE REVIEW			13
	2.1			22
	2.2			23
	2.3			23
	2.4			23
	2.5			29
	2.6			37
CHAPTER III	SCOPE OF PRESENT INVESTIGATION			39
CHAPTER IV	OBJECTIVES			41
CHAPTER V	EXPERIMENTAL PROCEDURE			43
	4.1			43
	4.2			46
	4.3			47
	4.4			47
	4.5			49
		4.5.1		49
		4.5.2		49
		4.5.3		50
		4.5.4		51
		4.5.5		52
CHAPTER V	RESULT AND DISCUSSIONS			
	5.1			54
	5.2			56

	5.3				58
		5.3.1			59
			5.3.1.1		64
		5.3.2			64
		5.3.3			68
	5.4				71
		5.4.1			71
		5.4.2			74
		5.4.3			75
	5.5				77
		5.5.1			77
		5.5.2			80
		5.5.3			82
	5.6				84
		5.6.1			84
		5.6.2			86
		5.6.3			87
	5.7				88
		5.7.1			88
		5.7.2			89
	5.8				96
		5.8.1			96
	5.9				98
		5.9.1			98
		5.9.2			101
	5.10				103
	5.11				106
CHAPTER VI	CONCLUSIONS				107
CHAPTER VII	SCOPE FOR FUTURE WORK				109
	LIST OF PUBLICATIONS				111
	REFERENCES				112

LIST OF FIGURES

Figure No.	Description	Page No.
Figure 1	Cu-Zn Equilibrium diagram	3
Figure 2	Mn-Si Equilibrium diagram	8
Figure 4.1 (a)	Raw material used for preparation of RB031	44
Figure 4.1 (b)	RB031 casting	45
Figure 4.2 (a)	Raw material of RB032	45
Figure 4.2(b)	Casting of RB032	45
Figure 4.3 (a)	Raw material of NAB(AB2)	46
Figure 4.3(b)	Casting of NAB(AB2)	46
Figure 4.4	Induction furnace used for manufacturing of alloys	48
Figure 4.5	Tilt position of Permanent Mould	48
Figure 4.6	Shell Mould packed for pouring	48
Figure 4.7	OLYMPUS microscope BX51M	49
Figure 4.8	Scanning electron microscope	50
Figure 4.9	Philips XPERT-3	51
Figure 4.11	Micro hardness tester	51
Figure 4.12	Pin on disc apparatus	52
Figure 4.13	Wear test specimen	53
Figure 4.14	Wear test specimens of Alloys fabricated	53
Figure 5.1A	Optical photographs of RB031 alloy under Shell Moulding	60
Figure 5.1B	Optical photographs of RB031 alloy under Permanent Moulding	61
Figure 5.2A	Optical photographs of RB032 alloy under shell moulding	66
Figure 5.2B	Optical photographs of RB032 alloy under permanent moulding	67
Figure 5.3A	Optical photographs of NAB(AB2) alloy under shell moulding	69
Figure 5.3B	Optical photographs of NAB (AB2) alloy under Permanent moulding	70
Figure 5.4	Grain size comparison graph	77

Figure 5.5A	SEM/EDAX images of RB031 alloy (Permanent Moulding)	78
Figure 5.5B	SEM/EDAX images of RB031 alloy (Shell Moulding)	79
Figure 5.5C	SEM/EDAX images of RB032 alloy (Shell Moulding)	80
Figure 5.5D	SEM/EDAX images of RB032 alloy (Permanent Moulding)	81
Figure 5.5E	SEM/EDAX images of NAB(AB2) alloy (Shell Moulding)	82
Figure 5.5F	SEM/EDAX images of NAB (AB2) alloy (Permanent Moulding)	83
Figure 5.6a	XRD image of RB031- Permanent Moulding	85
Figure 5.6b	XRD image of RB031- Shell Moulding	85
Figure 5.6c	XRD image of RB032- Permanent Moulding	86
Figure 5.6d	XRD pattern of RB032- Shell Moulding	87
Figure 5.6e	XRD image of NAB(AB2) alloy	88
Figure 5.7a	Microhardness comparison graph	89
Figure 5.7(b)	Variation of strength of alloys under Shell moulding condition	90
Figure 5.7(c)	Variation of strength of alloys under Permanent Moulding condition	91
Figure 5.7(d)	Variation of ductility of alloys under Shell Moulding condition	92
Figure 5.7(e)	Variation of ductility of alloys under Permanent Moulding condition	93
Figure 5.7f	Comparison of strength of alloys under Shell and Permanent Mould conditions	94
Figure 5.7g	Comparison of ductility of alloys under Shell and Permanent Mould conditions	95
Figure 5.8A	Effect of load on COF before heat treatment	96
Figure 5.8B	Effect of sliding velocity on COF before heat treatment	97

Figure 5.8C	Effect of load on wear rate before heat treatment	98
Figure 5.8D	Effect of sliding velocity on wear rate before heat treatment	99
Figure 5.9	Comparison of wear rate among three alloys	100
Figure 5.10	Comparison of Coefficient of friction(μ) among three alloys	100
Figure 5.11A	Effect of load on COF after heat treatment.	101
Figure 5.11B	Effect of sliding velocity on COF after heat treatment.	101
Figure 5.11C	Effect of load on wear rate after heat treatment	102
Figure 5.11D	Effect of sliding velocity on wear rate after heat treatment	102
Figure.5.12	Variation in worn Surfaces of alloys with increased Load	103
Figure.5.13	Variation in worn Surfaces of alloys with increased Load	105
Figure.5.14	Variation in worn Surfaces of alloys with increased Load	106

LIST OF TABLES

TABLE NO.	DESCRIPTION	PAGE NO.
Table 2.1	Silicides formed in Manganese Bronzes along with their melting points	13
Table 2.2	Composition of UNS Manganese Bronze alloys	14
Table 2.3	Mechanical property of cast UNS Manganese Bronze alloys and some common Bearing alloys	15
Table 2.4	Typical list of alloys and their properties selected for substitution with the developed alloy	15
Table 2.5	Variation of Zinc content on the Microstructure of Copper-Zinc alloys [41]	16
Table 2.6	variation of Zinc equivalent of Manganese Bronze alloy within the specification limits	16
Table 2.7	Zinc equivalence values of added element to Manganese Bronzes	16
Table 2.8	use of Zinc Equivalence in determining the zinc equivalent of an alloy	17
Table 2.9(a)	composition of an alloy for it estimating its mechanical properties from Ellis' curves	18
Table 2.9(b)	The accuracy of estimates of strength and elongation is shown by the following average of 36 tests (due to Ellis)	19
Table 2.10	comparison of microstructure estimated by the use of zinc equivalent with that obtained by microscope	20
Table 2.11	Variation of Mechanical properties with microstructure	20
Table 11(a)	S.T.A-7- C.X-3 (Admirally propeller Brass)[52]	22
Table 11(b)	H.S.B-44 (High Aluminum alloy)[52]	22
Table 4.1	Comparison of the actual composition of the different alloys made.	44
Table 4.15	Specifications of Scanning electron microscope	50
Table 4.16	Specifications of Micro Hardness Tester	52
Table 4.17	Specifications of Pin-on disc machine used for wear studies.	53
Table 5.1a	Chemical Composition of RB031	57

Table 5.1b	Chemical Composition of RB032	57
Table5.1c	Chemical Composition of NAB(AB2)	58
Table 5.2 a	Variables used in testing by Optical Microscopy (Shell Moulding)	59
Table 5.2b	Variables used in testing by Optical Microscopy (Permanent Moulding)	59
Table 5.3a	Variables used in testing by Optical Microscopy of RB032 alloy (Shell Moulding)	64
Table 5.3b	Variables used in testing by optical microscopy of RB032 alloy (Permanent moulding)	65
Table 5.4a	Variables used in testing by Optical Microscopy of NAB(AB2) alloy in Shell Moulding	68
Table 5.4b	Variables used in testing by Optical Microscopy of NAB(AB2) alloy in Permanent Moulding	68
Table 5.5a	Grain size measurements of RB031 alloy (Permanent Mould)	72
Table 5.5b	Grain size measurements of RB031 alloy (Shell Mould)	72
Table 5.6(a)	Grain size measurements of RB032 alloy (Shell mould)	74
Table 5.6(b)	Grain size measurements of RB032 alloy (Permanent mould)	74
Table 5.7a	Grain size measurements of NAB (AB2) alloy (Shell Mould)	75
Table 5.7b	Grain size measurements of NAB (AB2) alloy (Permanent Mould)	75

Chapter-1

INTRODUCTION

Copper alloys are chosen for design of bearing materials because they are good as mating surfaces. The conventional alloys of copper are Copper-Tin Bronzes, Aluminum-Bronzes and Manganese-Bronzes. Functionally the alloys are chosen based on load and lubrication. The first two are purely bearing materials while the last two are structurally strong alloys. The strength of Manganese Bronzes is comparable to that of low Carbon steel, has good Wear Resistance and superior Corrosion Resistance. Manganese Bronzes are severally called as high Tensile Brasses and High Strength Yellow Brasses. These are complex alloys with Copper and Zinc as the major constituents with additions of Aluminum, Iron and Manganese. Wear Resistance and strength are improved in alloys due the elements present. Presence of Silicon improves the Strength, Lubricity and Corrosion Resistance of the alloy [1]. The addition of different elements like Al, Fe, Mn and Si alters the room temperature properties as these elements have effects similar to Zinc to varying degrees. The chemistry of Manganese Bronzes shows presence of Al, Mn and Fe for strengthening the alloy. The Zinc percentage is substituted with Zinc equivalent which helps in predicting phases present at room temperature. Practically it is observed that a Zinc equivalent between 47% and 49% will result in desired properties without brittleness. With the need to keep Zinc as low as possible and add elements which will increase Apparent Zinc to the desired range of Zinc equivalent, small additions of Fe, Mn and Al are made. Further, Silicon in the right ratio with Manganese is needed to form Manganese Silicide particles which enhance Wear Resistance of the alloy [2]. The alloys developed will withstand loading pressures up to 200MPa, be highly wear resistant and can be subjected to high shock loading. It can also be employed for applications under high Unit loads and moderate Surface Loads. The high Hardness Ratio of 10:1 is obtained due to presence of manganese silicide particles in α+β phase matrix [2]. This high hardness ratio along with a low Co-efficient of dry friction is the reason for the excellent wear resistance. The presence of Silicon and Manganese helps in strengthening the alloy through the formation of inter-metallic Manganese Silicides. The ratio of Silicon to Manganese is critical to form the correct Manganese Silicide Intermetallic compound to achieve the required mechanical properties [3]. It is seen from the Cu-Zn equilibrium diagram [4] that up to 32.5% Zinc, the room temperature microstructure is α which is a solid solution of Zinc in Copper. Above 32.5% Zinc and up to 37.0% the Microstructure consists of α and β

phases. Between 39% to 56.5% zinc, the structure is wholly β' which is the ordered state of β at room temperature. Above 50.0% Zinc the brittle γ phase appears and renders the alloy very brittle and unfit for industrial applications. These structures are applicable to equilibrium state of cooling and with the solidification obtained in actual casting practice the various phases appear at lower Zinc values especially with the fast-cooling process.

This investigation covers the development aspects in two, Cast Manganese Bronze alloys with Silicon which will have comparable properties but will be less expensive than conventional alloys. It has been the aim of this investigation to synthesize RB031 (Cu-59.3%, Zn-34.85%, Mn, Al, Si, Fe, Sn, Pb, Co, Zr, Ni) and RB032 (Cu-63%, Zn-22.1%, Mn, Al, Si, Fe, Sn, Pb, Co, Zr, Ni) alloys which are Manganese Bronzes (High Tensile Brasses) corresponding to specification BS1400 HTB1 and HTB2 and ASTM505, B505B22, CDA86500, C86400, DINEn:1982 C763, CC7625. Synthesis has been carried out by induction melting and casting in Permanent and Shell moulds. Obtaining optimum values of zinc equivalent resulting in an optimum Microstructure, yet retaining high Mechanical properties has been dealt with in detail in this study. For the purpose of comparison, the alloy Nickel Aluminum Bronze (NAB-AB2 alloy) (Cu-82%, Al-8.65%, Mn, Si, Fe, Sn, Pb, Co, Zr, Ni) has been chosen and its characteristics also determined.

Chapter-2

LITERATURE REVIEW

From the literature review on high tensile brasses, it is very clear that since it is a complex alloy of copper and zinc with other alloying elements, zinc equivalent (ZE) is an important criterion to determine its microstructure and mechanical properties. Since there are lots of discrepancies amongst the various investigations on the suitable value of zinc equivalent while synthesizing manganese bronze alloys, it has become necessary to optimize the value of ZE for the alloys and its correlation with microstructure and mechanical properties for the same. Maintaining the correct value of ZE will result in in desired properties without brittleness. The intent of present investigation in the alloy development of RB031, RB032 and NAB (AB2) alloys has been to ensure that the value of ZE does not exceed 50% and the bottom limits of the chemistry also meet the property values without brittleness even in fast solidification processes like permanent mould and shell mould casting with not so fast a solidification process. NAB(AB_2) alloys, their synthesis and characterization have been taken up in the present study for the purposes of comparison with RB031 and RB032 alloys.

P.R. Dhar and S.K. Biswas [5] in their work on High Tensile Brass castings bring out clearly the distinction between α, β and γ phases in the Microstructure of these alloys. According to them the α phase consists of crystals of solid solution of Zinc in Copper. Brass acquires maximum relative elongation when the structure is completely α phase. β phase is also a solid solution but here the solvent is an electron compound of Cu-Zn. β phase is a disordered structure at high temperature which upon cooling acquirers an ordered structure β'- phase and crystals of excess α or γ phase precipitates from the solution. γ phase formed in high Zinc alloys is a solid solution of Cu and Zn having a complex cubic lattice, γ phase is a brittle component and brasses for room temperature services consist of either completely α- phase or β- phase. When γ- phase appears, the relative elongation is reduced.

Tom Nielson [6] in his studies on UNS86300 Manganese Bronze and the effect of composition on physical properties found that as the Zinc content increases significantly over 32.5% the α crystals cannot hold all the Zinc atoms in solid solution, instead as the alloy freezes, a new crystal phase solidifies. This β phase can hold up to 55% Zn in solid solution, just under the freezing point. Between 39% and 45.5% Zn, the β as it cools, will develop α crystals at grain boundaries. The presence of β crystal strengthens the alloy by resistance to

deformation. Somewhere between 46% ZE and 57% ZE will be the composition that will provide the required physical properties.

Keicchiro Oishi, Isao Saraki, and Junichi Otani [7] studied the refinement of copper alloys with silicon additions and emphasized the importance of Grain refinement in relation to strength of metals. They found out that strength can be increased by developing a metal/alloy with a fine recrystallized structure, and by accumulation of strain energy.

Hamid Doost, Mohammadi and Hamid Moridshai [8] while studying the effect of Silicon on properties of a $Cu_{60}Zn_{40}$ alloy found that presence of Silicon helps in promoting the β' phase formation and the microstructure changed from duplex α+β' phase to β' phase. They also found that a reduction of stacking fault energy reduces grain size as well as Microstructural variation.

M. Sadayappan, D. Cousineau, R. Zavadil, M. Sahoo and H. Michels [9] while investigating on the grain refinement of Permanent Mold cast Copper-Base alloys came up with the revelation that the grain refinement behavior of Cu-Zn alloy is influenced by various alloy additions such as Tin, Aluminum and Lead. It was found that Boron refined both the Yellow Brasses whereas Zirconium was found to be effective for all four Copper alloys.

Reif [10] found that Zirconium, Magnesium, Iron and Phosphorous help in the formation of a more equiaxed structure, prolonged holding high melt and/or mould temperatures help in grain refinement of copper alloys with 25-42% Zinc.

Romankiewicz F., Eflebrok, R, Englers.,[11] found that in sand cast and Permanent mould cast 70Cu-30Zn alloy, Zirconium served as an effective grain refiner and resulted in good mechanical properties of castings.

Fasoyinu F.A., etal., [12] found a profound effect of grain refinement on fluidity of the alloys.

M. Sadayappan, J.P. Thomson, M. Elboujdaini, G. Ping Gu [13] while studying grain refinement of Copper alloys Cast in Permanent Moulds found that zirconium was an effective refiner for the four alloys investigated.

A. Waheed and N. Ridley [14] while studying the effect of heat treatment on wear behavior of high tensile brasses found that it depended on the volume fraction of α and β phases, on

their distribution in the microstructure and on the ease with which the hard Mn_5Si_3 particles became detached from the phases in which they were located.

One of the aims of this investigation has been to establish relationship between wear parameters and material properties of the high tensile brasses which were produced by permanent and shell mould casting methods. Dry sliding pin on disc wear tests were performed against an AISI-52100 steel counter face. After the wear tests the worn surfaces of the pins and wear debris are studied by Scanning Electron Microscopy combined with EDAX analysis. This is done to get a better understanding of the characteristics, wear mechanisms and tribological behavior of Manganese Bronze material under dry sliding conditions.

Grain refinement behavior of copper alloys cast in Permanent moulds is one of the least studied subjects in copper alloy castings. This effect would be in casting varying section size where their cooling rate differ from section to section. Different section sizes may reveal different grain sizes after grain refinement. The present studies reveal that this has been achieved more so in permanent moulded samples of RB031, RB032 than NAB (AB_2) alloys. The RB032 permanent moulded alloy in particular has more refined recrystallized grains with increase in number of nucleation sites and also there is inhibition of grain growth and this accounts for the increase its strength levels of this alloy. Additions of Zirconium has refined the grain structure and morphology of RB032 alloy in Permanent mould castings.

Chapter-3

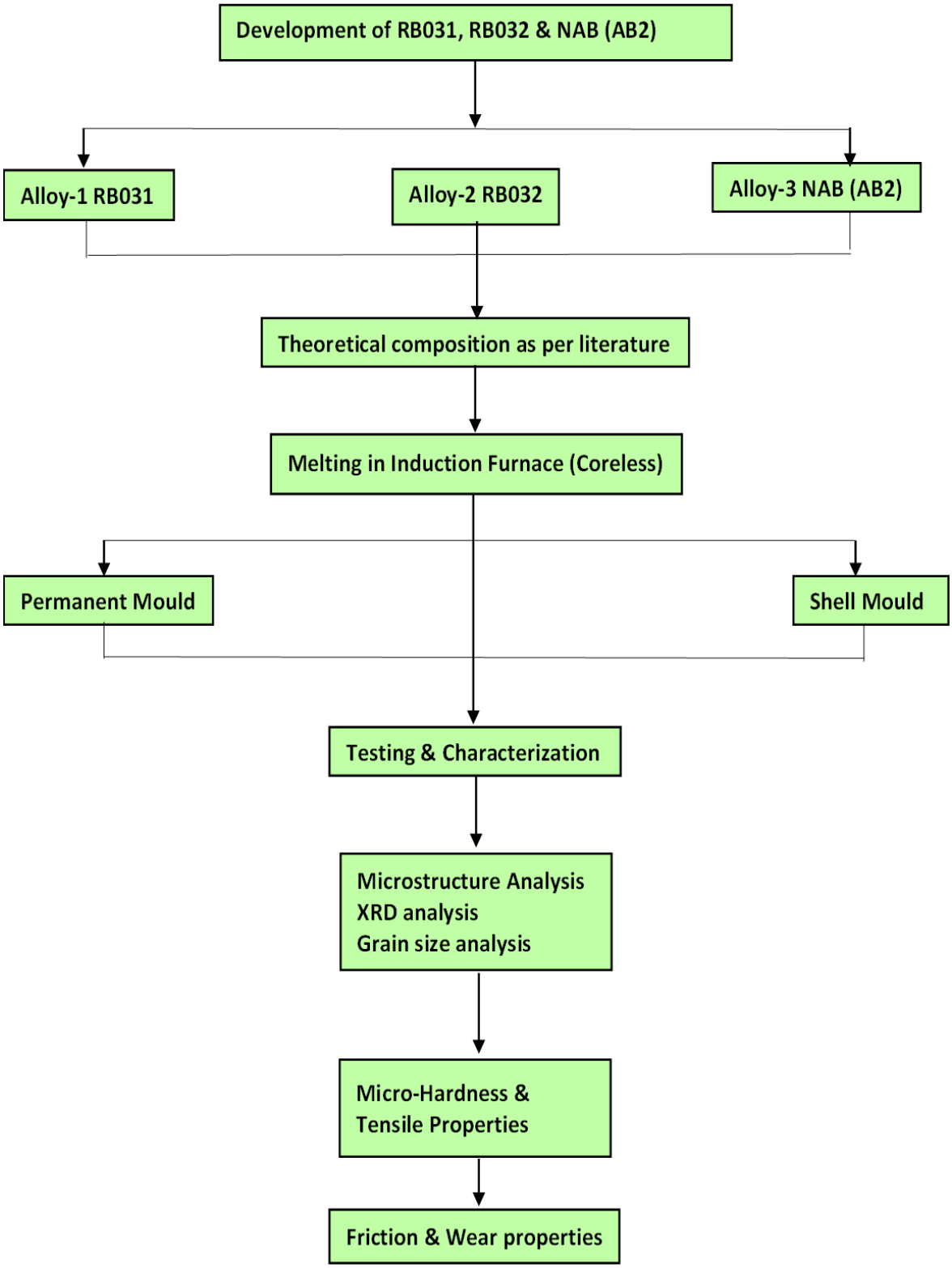
OBJECTIVES

The objectives of a present investigation are as follows

- To develop high quality RB031 copper casting alloy by Induction Melting in a Coreless Medium Frequency Induction furnace by permanent and shell mould method.
- To develop high quality RB032 Copper Casting alloy by Induction melting in Coreless Medium Frequency Induction furnace by permanent and shell mould method.
- Induction Melting of NAB (AB2) alloy of standard specification and Casting it in Permanent and Shell Moulds.
- To characterize Microstructure, Grain Size Measurement, Hardness and Mechanical Properties of developed castings by Optical Microscopy SEM/EDX and XRD measurements of the castings in the Un-heat-treated condition with Zirconium as modifier used in melting.
- To evaluate and compare the Microstructure, Grain Size Measurement, Mechanical property measurements of RB031, RB032 and NAB(AB2) castings in the Heat-Treated condition without Zirconium additions using Optical microscopy and SEM/EDX and XRD measurements of the castings in this condition.
- To study Tribological characteristics of RB031, RB032 and NAB (AB2) alloy by wear studies using Pin-On-Disc method of Wear test.
- To identify Wear/ material removal mechanism on Wear surfaces of developed castings using optical microscopy SEM/EDX techniques for RB031, RB032 and NAB (AB2) alloys.
- To evaluate and compare the behavior of developed castings of RB031, RB032 and NAB (AB2) alloys both before Heat Treatment and after Heat treatment of the castings with and without zirconium added as modifying element during melting of the alloys.

Chapter-4

EXPERIMENTAL PROCEDURE



Chapter-5

RESULTS AND DISCUSSIONS

This investigation has aimed at modifying the microstructures of RB031 and RB032 alloys using zirconium metal as a modifier and by heat treatment studying the suitability on the types, forms and distribution of phases within the matrix and their effects on the mechanical properties. Results obtained in this work are grouped under the following headings and are discussed.

5.1 Microstructure of RB031alloy

The microstructure consists of α particles dispersed in the matrix of copper solid solution. Further, the structure contains α and β phases with manganese silicide intermetallic particles distributed finely in β matrix. Since the structure is not completely α phase, maximum relative elongation in the alloy is low. The β phase present in this alloy is a disordered structure at higher temperature which upon cooling has reduced to β’ which is more ordered at lower temperatures. This phase is hard and brittle. The microstructure of this alloy with zirconium addition reveals Mn-Si particles distributed in β matrix. Heat treatment of the castings has resulted in reduction of particle size and distribution of fine Mn-Si particles in β matrix. In the presence of zirconium modifier growth of Mn-Si particles is inherited during heat treatment. In permanent moulds: growth of Mn-Si particles is inhibited during heat treatment and the particles are small and of short length dispersed in β matrix.

5.2 Microstructure of RB032 alloy

Microstructure consist of particles dispersed in the matrix of copper solid solution. The structure reveals the formation of Fe3Si3 and Mn5Si3 silicides, also the dark dendrites of an α phase in a matrix of β equiaxed grains. Further, it shows light itching areas of α which have a widmanstatten morphology a darker etching matrix of β phase and rod-shaped Mn5Si3 particles with hexagonal cross section. The Grain structure in permanent moulds has changed from columnar to fine equiaxed since the iron content is more. This is due to precipitation of secondary iron rich phase in the iron enriched liquid at some point during solidification exactly enough to nucleate further β grains. Iron precipitated during solidification as primary γ iron dendrites when the Ion concentration is more than 1% it and that these iron dendrites then nucleate the α or β solid solution grains. When the iron content and casting conditions are such that the grain structure is columnar no iron rich nuclei is precipitated before

solidification of β start that is either the composition lies below the peritectic point or the iron rich phase has undercooled until after the solid solution grains have appeared. Nickel with aluminum creates intermetallic phase which has a precipitation hardening effect. Manganese is dissolved in α phase and has an effect similar to iron.

5.3 Microstructure of NAB(AB2) alloy

Microstructural analysis has revealed the primary α phase intermetallic phases and find stable reinforcing κ-phase and these alterations in the phase have resulted in the development of Mechanical properties. Heat treatment of Nickel aluminium bronze samples has resulted in greater homogeneity in their microstructure and general refinement of the grains. The presence of dendritic structure was noticed in the cast material which is not there after heat treatment procedure. Further the presence of κ-phase which is a combination of Fe3Al and Ni-Al precipitate is seen microstructure and this is more true in heat treated samples. Aging of the samples during heat treatment has resulted in formation of martensite structure and this has enhanced the strength of material.

5.4 Grain size studies

- The % difference in grain size among RB032 and NAB alloys is 41% under shell mould condition and 67% under permanent mould condition.
- The % difference in grain size among RB031 and RB032 alloys is 80% under shell mould condition and 90% under permanent mould condition.

5.5 XRD Analysis

Due to small concentration of elements present such as Ni, Mn and Zr, the reflections of these elements in the XRD are not identified whereas the presence of these elements through EDS measurement has been confirmed in all the alloys made. All peaks correspond to copper. There is slight shift in values of 2θ. There are peaks at 2θ- 43.54° (111), 50.72° (200) and 74.56° (220) with intensity. There is a minor peak to left of major peak at 43.54° due to Zn metal.

All peaks correspond to copper. Slight shift in value of 2θ is noticed. A minor peak is seen to the left of major peak.

There are two major peaks at 2θ-43° representing Cu and Zn. Due to less crystallinity in the material peaks are not very sharp. Figure 5.12 shows the XRD image of NAB(AB2) alloy.

5.6 Mechanical Properties

5.6.1 Hardness

It can be seen that there exists 12.18% difference in hardness value between RB031and RB032 in Permanent mould condition, 7.25% in shell mould condition and 7.96% difference between RB032 and NAB (AB2) alloy in Permanent mould condition, 3.67% in shell mould condition. Thus, indicating higher strength in RB032 alloy when compared to other two alloys.

5.6.2 Tensile Properties

The % difference in yield strength among RB031, RB032 is 3.52% in Shell mould condition and 16.32% in Permanent mould condition; whereas the % difference in yield strength among RB032, NAB is 15.3% in Shell mould condition and 38.7% in Permanent mould condition. Thus, indicating the superiority of RB032 alloy in Permanent mould condition when compare with other two alloys.

Among all the three alloys studied RB032 demonstrated superior tensile characteristics compared to the other two. Addition of zirconium has significantly improved the ultimate tensile strength and yield strength of RB031, RB032 alloys. The higher tensile strength, higher yield strength, ductility and hardness values in permanent moulded RB032 alloy is to grain refinement during fast solidification process or chilling action in moulds, precipitation hardening Quenching and subsequent ageing of the samples during heat treatment has resulted in the formation of martensitic structure β and this has enhanced the strength of the material of the alloy in permanent moulded samples. In the case of NAB (AB2) alloy the increase in strength in shell moulded casting can be explained by the presence of K (kappa) phase.

The % difference in yield strength among RB031, RB032 is 3.52% in Shell mould condition and 6% in Permanent mould condition; whereas the % difference in yield strength among RB032, NAB is 21% in Shell mould condition and 45% in Permanent mould condition. Also, it is seen from the graph that the % difference in Tensile strength among RB031, RB032 is 1% in Shell mould condition and 2% in Permanent mould condition; whereas the % difference in Tensile strength among RB032, NAB is 2% in Shell mould condition and 11% in Permanent mould condition. the graph also indicates that the % difference in Elongation among RB031, RB032 is 2% in Shell mould condition and 33% in Permanent mould

condition; whereas the % difference in Elongation among RB032, NAB is 74% in Shell mould condition and 72% in Permanent mould condition.

5.7 Tribological Properties

5.7.1 Coefficient of Friction

- **Effect of Load**

The COF for all the three alloys is seen to decrease with increase in load under both conditions and when compared to shell mould condition the COF is found to be comparatively low in permanent mould condition.

- **Effect of Sliding Velocity**

The COF for all the three alloys is seen to increase with increase in sliding velocity under both conditions and when compared to shell mould condition the COF is found to be comparatively low in permanent mould condition.

5.7.2 Wear rate

- **Effect of Load**

The wear rate seems to increase with increase in load for all the three alloys under both conditions and when compared to shell mould condition the wear rate is found to be comparatively low in permanent mould condition.

- **Effect of Sliding Velocity**

The wear rate is found to increase with increase in sliding velocity for all the three alloys under both conditions and when compared to shell mould condition the wear rate is found to be comparatively low in permanent mould condition.

CONCLUSIONS

In the present investigation, the following conclusions are made;

- RB031 and RB032 copper alloys were successfully synthesized using Induction Melting Medium Frequency Induction furnace by permanent and shell mould methods.
- From the microstructures of RB031 and RB032 alloys particularly of Permanent Moulded castings the delicate balance of the proportions of **α** and **β** phases in their microstructure has made them stronger at elevated temperatures (**β** phase property). Further, Heat treatment of these alloys has modified the determination of phases as well as improvement in their physical properties.
- The challenge of controlling the alloying elements such as aluminum and manganese and making a defect free casting of RB031 and RB032 alloys with optimized strength and wear behaviour comparable to NAB(AB2) alloy has been accomplished in this study.
- Coarseness of **β** grains is directly related to the slow cooling in shell moulded castings. Very fine Manganese Silicide needles in a uniformly fine grained **β** matrix is the reason for the higher Mechanical Properties in Permanent Moulded samples of RB032 alloy. The fine-grained structure is due to the very fast Solidification achieved in Permanent Moulded samples.
- Heat treatment of RB031 and RB032 alloy castings has stabilized the matrix and resulted in higher uniformity in the microstructure of alloys as well as overall refining of the grain structure.
- When the samples were aged during heat treatment, the formation of martensitic structure (β) occurred, which resulted in an increase in the strength of the Permanent Moulded alloy. In a fine-grained matrix of α+β phases, there is a homogeneous distribution of intermetallic Manganese Silicide.
- The NAB (AB2) alloy is showing less strength values in terms of Ultimate tensile strength, Yield strength compared to RB032 alloy developed. However, the ductility values of NAB (AB2) alloy do not seem to be decreasing very much.
- Two alloys (viz. RB031 and RB032) with Zinc Equivalent have led to optimum microstructure and yet retain the high Mechanical Properties in the alloys.

- It is necessary to refine recrystallized grains of metals from an approach of material properties like enhancement of strength values. The present study reveals that this has been achieved more so in Permanent Mould samples of RB031 and RB032 manganese bronze alloys than NAB (AB2) alloys.
- The RB032 permanent mould alloy in particular has more refined recrystallized grains with increasing number of nucleation sites and also there is inhibition of grain growth and this account for the increased strength levels of this alloy.
- Additions of Zirconium as a grain refiner has refined the Morphology and Microstructure of RB032 alloy in Permanent Mould casting.
- The high value of Zinc Equivalent (ZE) at the low limit prevents the formation of a high proportion of soft α phase and at the top limit of the composition, the ZE value is not high enough for the formation of brittle Gama phase. The additions of Si and Mn have resulted in strengthening the RB031 & RB032 alloys through the formation of Inter metallic Manganese Silicides.
- Good Mechanical Properties and Wear Resistance of the material of the alloy can be achieved by correct Silicon to Manganese ratio in the intermetallic compound Manganese Silicide and this has been clearly demonstrated in both RB031 and RB032 alloys.
- Manganese Silicide particles formed in a matrix of α+β phase composition resulted in a high hardness ratio of 10:1 due to the development of Manganese Silicide particles. Because of the high hardness ratio, along with the low coefficient of dry friction, this material has outstanding wear resistance and durability.
- Zinc Equivalent (ZE) is an important Criterion to determine the microstructure and Mechanical Properties. By setting the aim points for chemistry within the specification range, different room-temperature microstructures one possible in the alloys developed.
- The NAB (AB2) alloy available in the market per kg basis is more expensive than the RB031 and RB032 alloy among the Manganese Bronzes developed in this investigation. Hence the High Tensile Brasses or Manganese Bronzes have very high potential to replace the more expensive tin bronzes and Aluminum bronzes for various applications such as bearings and structural parts.

REFERENCES

1. P. Sriram, “Cast Manganese Bronze with Silicon - a versatile alloy publication and presentation - CIIFIFEX - 2018, at Gandhinagar India, copyright 2012, American Foundry Society.
2. P. Sriram, “High Strength Manganese Bronze With Silicon - Development And Testing”, Institute of Indian Foundrymen Annual Convention, Ahmedabad Jan 2018.
3. P. Sriram, “Copper Alloy Foundries Present and Future”, Indian Journal of Foundry, vol 6, no 3, pp 10-12.
4. M. Hansen and K. Anderko, “Constitution of Binary Alloys,” 2nd edition, McGraw-Hill companies, Inc., New York, 1958.
5. P.R. Dhar, S.K. Biswas, “High Tensile Brasses”, paper presented at ICDC silver jubilee symposium held in Bengaluru, 14-15 February 1991 pp 1-5.
6. Tom Nielson, “Manganese Silicide Formation in Manganese Silicon Brass” Report of Lakeside Industrial Products, USA February 11, 2009.
7. Keicchiro Oishi, Isao Sasaki, Junichi Otani, “Effect of Silicon Addition on Grain Refinement of Copper Alloys”, Materials Letters, 57(2003) 2280-2286.
8. Hamid doost, Mohammadi, Hamid Moridshai, “Effects of Silicon on the Microstructive Ordering Transformation and Properties of $Cu_{60}Zn_{40}$ Alloy”, Journal of Alloys and Compounds (2015) 33865 p1-17.
9. M. Sadayappan, D. Cousineau, R. Zavadil, M. Sahoo, H.T. Michels, “Grain Refinement of Permanent Mold Cast Copper Base Alloys”, AFS Transactions, vol 110, pp 505-514, 2002.
10. Weber G, Rief. W, “Grain Refining of Metals”, Metall, US Patent no.4, vol.41, pp1131-1137 (1987).
11. Romankiewicz F, Eflebrok, R. Englers, “Effect of Grain Refinement by Zirconium on The Morphology of Solidification, Feeding Capacities and Mechanical Properties of Brass Cu-Zn30 and Silicon Brass CuZn15Si4”, Gissereiforschung, vol.39, pp 23-33 (1987).
12. Fasoyinu, F.A., et.al., “Effect of Grain Refinement on The Heat Resistance and Shrinkage Characteristics of Permanent Mold Cast Yellow Brass (C85800)”, Afs Transactions, vol. 106, 1998.
13. M. Sadayappan, J. P. Thomson, M. Elboujdaini, G. Ping Gu, “Grain Refinement of Permanent Mold Cast Copper Base Alloys”, Final Report, MTL report 2004-6 (tr-r) April 2004.
14. K.Waheed, N.Ridley, “microstructure and wear of some high tensile brasses”, journal of material science 29 (1994) 1692-1699.

PUBLICATIONS

1. **Prabhakar Kuppahalli**, R Keshavamurthy, P Sriram, Ahobal N, "Influence of Silicon Additions on Microstructure and Mechanical Properties of Manganese Bronze Alloys", *Iranian Journal of Materials Science and Engineering*, 18 (2) 2021.
2. **Prabhakar Kuppahalli**, R Keshavamurthy, P Sriram, T J Kavya, "Microstructure and mechanical behaviour of Nickel Aluminum Bronze Alloys", *IOP conference series: Material science and Engineering*, 577(012044), 2019.
3. **Prabhakar Kuppahalli**, "Mechanical Characteristics of High Tensile Brasses with Silicon Additions", *International Conference on Advanced Materials and Processes for Defence Applications*, Hyderabad, September 23,2019.
4. **Prabhakar Kuppahalli**, R Keshavamurthy, P Sriram, Ahobal N, "Friction and Wear behaviour of High Tensile Brasses or Manganese Bronzes with Silicon additions", *Virtual International Conference on Recent Advances in Chemical and Biological Sciences*, December 9,2020.

Dr. R KESHAVAMURTHY

Professor & HOD
Department of Mechanical Engineering

DSCE, Bengaluru

Professor & HOD
Department of Mechanical Engineering
Dayananda Sagar College of Engineering
Kumaraswamy Layout, Bangalore - 560078

Dr. K ANANTHARAJU

Director
Dr. D Premachandra Sagar Centre for Advanced Materials
DSCE, Bengaluru

Dr. K.S. Ananth a Raju
Director
Dr. D. Premachandra Sagar Centre
for Advanced Materials
DSCE Campus, Bengaluru 560 078.